Metal–Oxo Photo-oxidants. Photochemistry and Photophysics of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) and *trans*-$[Os^{VI}(CN)_4(O)_2]^{2-}$

Chi-Ming Che,*[a] Vivian Wing-Wah Yam,[a] Kar-Cheong Cho,[b] and Harry B. Gray[c]

[a] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong*
[b] *Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*
[c] *Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125, U.S.A.*

trans-$[Os^{VI}(tmc)(O)_2]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) and *trans*-$[Os^{VI}(CN)_4(O)_2]^{2-}$ are emissive in the solid state and in fluid solutions at room temperature ($\tau \sim 1.0$—1.5 μs); the ^3E_g state of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ is a powerful one-electron oxidant {$[Os^{VI}(O)_2]^{2+} + e^- \rightarrow [Os^{V}(O)_2]^{+}$, $E_f^0 > 2.0$ V *vs.* normal hydrogen electrode} in aqueous solution, reacting with PPh_3 and $(PhCH_2)_2S$ to give $O{=}PPh_3$ and $(PhCH_2)_2S{=}O$, respectively.

Relatively few long-lived electronic excited states of metal complexes are powerful oxidants.[1] Although metalloporphyrin and metal–bipyridine complexes are commonly employed as photocatalysts,[1f,h] these systems suffer from the disadvantage that long-lived excited states with potentials greater than 1.6 V (*vs.* normal hydrogen electrode, n.h.e.) are difficult to generate, because of the rapid intramolecular reductive quenching that occurs when π-unsaturated ligands are present. We describe here a new class of excited-state reagents that are powerful oxidants (~2 V *vs.* n.h.e.) in solution at room temperature.[1c,2]

The optical spectrum of *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$[3] (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) (and $[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$[4] in parentheses) in MeCN displays vibronically structured absorption bands at 312 (320) nm [$(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi^*})^1$, $^1A_{1g} \rightarrow {}^1E_g$]† and 355 (370) nm [$(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi^*})^1$, $^1A_{1g} \rightarrow {}^3E_g$].† Excitation of *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$ or $[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$ at 350—400 nm results in red emission; photophysical data are summarized in Table 1. The large difference in excitation and emission energies suggests that the emissive state is not E_g (^3E_g); it possibly could be either the B_{1g} or B_{2g} sublevel of ^3E_g.[1d,2a,3] Because neither the lifetime nor the intensity of the emission of *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$ is quenched by H^+ (Table 1), the OsO_2^{2+} species can be employed as a photo-oxidant in both protic and aprotic media. The reduction potential ($Os^{VI} + e^- \rightarrow Os^{V}$) of $[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$‡ is much more negative than that of *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$, −1.52 *vs.* −0.73 V[5] (*vs.* $cp_2Fe^{+/0}$; cp = cyclopentadienyl). Values of the standard reduction potential of the Os^{VI}/Os^{V} couple (0.01 V *vs.* n.h.e.)[3] and the estimated emission E_{0-0} (>2 eV)† for *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ suggest that its ^3E_g state [$(d_{xy})^1(d_{\pi^*})^1$] is an extremely powerful one-electron oxidant: $E_f^0[Os^{VI}(O)_2]^{2+*}/[Os^{V}O_2]^{+} > 2.0$ V (*vs.* n.h.e.) in H_2O (>1.4 V *vs.* $cp_2Fe^{+/0}$ in MeCN). The excited-state reduction potential of $[Os^{VI}(CN)_4(O)_2]^{2-}$ is estimated to be ~0.5 V *vs.* $cp_2Fe^{+/0}$ in MeCN, assuming its emission E_{0-0} is ~2 eV.† Thus a series of *trans*-dioxo-osmium(VI) photo-oxidants can be obtained by ligand variations.

trans-$[Os^{VI}(en)_2(O)_2][PF_6]_2$ (en = 1,2-diamineoethane) and *trans*-$[Os^{VI}(NH_3)_4(O)_2][PF_6]_2$,[6] whose optical spectra are virtually the same as that of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$, exhibited no emission in the solid state or in fluid solution. It is likely that hydrogen bonding between Os=O and N–H groups provides an efficient mechanism for nonradiative decay of the excited states of these complexes.[2a]

Steady-state quenching results for *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$ with substrates are set out in Table 2. The large

† $d_{\pi^*} = (d_{xz}, d_{yz})$; the A_{1g} and E_g symbols are for *trans*-$[ML_4(O)_2]$ complexes with D_{4h} symmetry: see refs. 2(a) and 3. The emission E_{0-0} was estimated from the emission spectrum. The Os–O stretching frequency in the ^3E_g state was estimated from the vibrational spacing in the $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi^*})^1$ transition. See also ref. 2(a).

‡ The cyclic voltammogram of $[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$ was obtained in 0.1 M-$[Bu_4N]PF_6$ acetonitrile solution, working electrode pyrolytic graphite. The Os^{VI}/Os^{V} couple at −1.52 V *vs.* $cp_2Fe^{+/0}$ is quasi-reversible with ΔE_p ~70 mV at a scan rate of 100 mV s^{-1}.

Table 1. Photophysical data for *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$ and $[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$.[a]

Complex	Emission[b] $\lambda_{max.}$/nm		Lifetime/μs	
trans-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$	Solid,	630	MeCN,	1.0
	MeCN,	630	H_2O,	1.4
			0.1 M-CF_3CO_2H,	1.5
$[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$	MeCN,	700(br)	MeCN,	0.4

[a] The quantum yield of the phosphorescence was $\leq 10^{-3}$ in both cases: standard, quinine sulphate. [b] The emission spectrum was run on a Hitachi 650—60 spectrophotometer.

quenching rate constants (3—4 × 10^9 dm^3 mol^{-1} s^{-1}) for amines are consistent with the substantial driving forces for the one-electron oxidation of $NR^1R^2R^3$ to $^+NR^1R^2R^3$. Flash photolysis of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ and tmpd (*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine) in degassed acetonitrile yields a transient $tmpd^+$ signal ($\lambda_{max.}$ ~ 600 nm)[7] that decays by second-order kinetics.

The high reduction potential of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+*}$ suggests that the excited-state reagent also can be employed for halide oxidations. Exciplex formation was not observed between *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ and X^- (X = Cl or Br). The difference in quenching rates of Cl^- and Br^- (a factor of 100: see Table 2) is parallel with the difference in their oxidation potentials and indicates that the photosystem might be useful for bromide analysis in the presence of chloride.

The Os–O bond in the ^3E_g state of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ or $[Os^{VI}(CN)_4(O)_2]^{2-}$ is much weaker than in the ground state [ν(Os=O): $^1A_{1g}$ ~ 870 cm^{-1}; ^3E_g ~700 cm^{-1}],† implying that these osmium complexes might undergo oxo-transfer photoreactions.[3] Oxygen-atom acceptors (stilbene, phosphine, phosphite, and dialkyl sulphide) quench the phosphorescence of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ at diffusion-limited rates (Table 2). The k_q values for *cis*- and *trans*-stilbenes cannot be explained by an energy-transfer mechanism, because the excited-state energy of the osmium complex (48 ± 3 kcal mol^{-1}; cal = 4.184 J)† is lower than the triplet energy of the organic quencher (*cis*-stilbene, 49; *trans*-stilbene, 57 kcal mol^{-1}).[8] Although photolysis (λ >300 nm) of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ and stilbene in degassed MeCN for 3 h produced no epoxide or benzaldehyde, O=PPh_3 and $(PhCH_2)_2$S=O (yield ~31%) were formed under similar photochemical conditions with PPh_3 and $(PhCH_2)_2S$. Similarly, O=PPh_3 was formed upon irradiation (λ >300 nm) of $[Ph_4As]_2[Os^{VI}(CN)_4(O)_2]$ and PPh_3 in MeCN for 3 h.§ The phosphorescence of $[Os^{VI}(CN)_4(O)_2]^{2-}$, which has a lower excited-state reduction potential than *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$, is not efficiently quenched by PPh_3 (k_q <10^6 dm^3 mol^{-1} s^{-1}). The relative rates of photo-oxidation of PPh_3 by the two $Os(O)_2^{2+}$ complexes suggest that electron transfer to $Os(O)_2^{2+*}$ is the initial step in the reaction pathway. The observation that O=PPh_3 is formed in these photoreactions confirms that oxygen-atom transfer[9] competes effectively with back electron transfer in the photogenerated $[Os(O)_2^+][PPh_3^+]$ complex.

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§ Steady-state irradiation was performed with a high-pressure mercury short-arc lamp (350 W) equipped with filters or monochromator. Photochemical reaction conditions: *trans*-$[Os^{VI}(tmc)(O)_2][PF_6]_2$, 6.5 mg; PPh_3, 100 mg; MeCN, 4 ml; *trans*-$[Os^{VI}(tmc)(O)_2][PF_6]_2$, 20 mg; $(PhCH_2)_2S$, 30 mg; MeCN, 4 ml. O=PPh_3 was identified by its i.r. band at 1190 cm^{-1}. $(PhCH_2)_2$S=O was identified by ^1H n.m.r. spectroscopy, δ 3.97 in $CDCl_3$ with *m*-toluic acid as the internal standard. The yield of $(PhCH_2)_2$S=O is based on the amount of osmium complex used. No O=PPh_3 or $(PhCH_2)_2$S=O was formed in the absence of the osmium complex.

Table 2. Rate constants for the quenching of 0.1 M *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ in degassed 0.1 M-$[Et_4N]ClO_4$ acetonitrile solution at 25 °C.

Quencher	k_q[a]/dm^3 mol^{-1} s^{-1}
tmpd	4.4×10^9
Ph_2NH	3.1×10^9
$PhNMe_2$	3.5×10^9
PPh_3	4.0×10^9
cis-Stilbene	2.1×10^9
trans-Stilbene	4.4×10^9
$(PhO)_3P$	1.2×10^9
Bu_3P	7.8×10^8
$(PhCH_2)_2S$	2.2×10^8
Et_2S	2.4×10^8
Thiophene	1.4×10^7
NaCl[b]	1.0×10^6
NaBr[b]	1.1×10^8

[a] The second-order quenching rate constants were obtained by both intensity and lifetime-quenching methods. [b] In 0.1 M-CF_3CO_2H.

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